Final Report for NASA grant NAGW - 1465

Support of the Harvard ClO/BrO Instrument for the Preparation, Execution, and Data Review for the Arctic Vortex Mission

Completion Date: 14 December, 1990

Principal Investigator: William H. Brune

Department of Meteorology
Pennsylvania State University
University Park, PA 16802

1 October, 1991

Two chemical species that are intimately involved in the destruction of ozone in the lower stratosphere are ClO and BrO. In, this work, we used the Harvard University ClO/BrO instrument, mounted on the NASA ER-2 aircraft, to study the abundances of these species in the Northern Hemisphere, particularly near the Arctic polar vortex in 1989 during the Airborne Arctic Stratospheric Experiment (AASE) mission in 1989. The scientific objectives were to understand the response of the chemical species to the changing environment of the wintertime polar stratosphere, and the potential effects that these changes in ClO and BrO abundances have on other species, particularly ozone.

The AASE mission was highly successful. The Harvard ER-2 instrument performed well during the fourteen flights toward the polar vortex from Stavanger, Norway, the four transit flights between Moffett Field, California and Stavanger, and the five test flights from Moffett Field. Results concerning the Arctic polar vortex and the lower stratosphere at midlatitudes have been gleaned from the resulting ClO and BrO data sets.

Perhaps the most important result was that the ClO abundances in the Arctic polar vortex were as large as those observed in the Antarctic ozone hole, with observed values exceeding 1.2 ppbv (greater than 30% of the total available chlorine). Enhanced levels of ClO were observed in early January, two months before the Spring equinox. Furthermore, calculations assuming thermal equilibrium between ClO and Cl_2O_2 in the dark polar stratosphere indicate that most, if not all, of the available inorganic chlorine had been shifted to ClO and Cl_2O_2 from HCl and $ClONO_2$ by mid-January between the potential temperatures of 390 K and 470 K. Thus, the heterogeneous processes that convert chlorine to reactive forms were efficient enough in 1989 that the conversion was essentially complete in early winter. As a result, enhanced amounts of ClO, capable in sunlight of the rapid destruction of ozone, were available in early winter and remained available into mid-February.

The BrO mixing ratios in the Arctic polar vortex were measured to be 8 ± 2 pptv, about twice the levels measured outside the vortex. These values in the Arctic chemically perturbed region were comparable to those measured in the Antarctic chemically perturbed region.

A modeling study that we performed showed that once the chlorine, bromine, and reactive nitrogen families have been thoroughly altered by the presence of PSCs, the de-

struction of 10% to 15% of the ozone in that air mass is virtually assured. Taken over the depth of the chemically perturbed region, this loss translates into a 5% to 8% loss in column ozone. This study also indicated that the time constant for ozone destruction in the Arctic polar vortex will decrease sufficiently in the future, as the chlorine abundance of the stratosphere increases, that large reduction of Arctic ozone, although somewhat unlikely at present, will become increasingly more likely.

Other studies were focused on the chemistry that might be occurring outside the Arctic polar vortex. A comparison was made between ClO data obtained outside the Arctic polar vortex and the results of calculations that included conversion chemistry on background sulfuric acid aerosols. The conclusion was that conversion of the chlorine from reservoir to reactive forms was inefficient on the global background sulfate aerosol layer at temperatures above the PSC formation temperature. This result was in agreement with the expectations from recent laboratory experiments. In a second study, ClO mixing ratios measured outside the Arctic polar vortex were found to be 150 pptv, the largest amounts ever measured at midlatitudes. Although these large values appeared to be associated with the heterogeneous chemistry inside the polar vortex, the seasonal trend of midlatitude ClO mixing ratios suggests that other chemistry in the midlatitudes may be occurring.

This grant supported travel to conferences, both national and international, during which the results from the AASE mission were discussed. The two international meetings were "Workshop on Recent Campaigns on Polar Ozone" at the XV General Assembly of the European Geophysical Society in Copenhagen, Denmark, and the International Meeting on Chemical Processes and Modeling of the Ozone Layer in Leningrad, USSR. This later meeting in particular was a valuable exchange of ideas and information.

Journal publications in which the support from this grant is recognized are listed in the bibliography entitled: "Journal Articles Supported by NAGW-1465". A large number of modeling studies that use the ClO and BrO data set have also been published, and several more are currently in press. Most of the published studies can be found in a special issue of *Geophysical Research Letters*. This issue is Volume 17, Number 4. Journal publications which use the ClO data set generated in part by this grant are listed in the bibliography entitled: "Journal Articles That Use the ClO and BrO Data."